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(54) COATING COMPOSITIONS

(71) We, HOECHST AKTIEN-GESELLSCHAFT, a German Body Corporation of 6230 Frankfurt/Main 80, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to coating compositions, particularly compositions for application to metal substrates to provide a protective coating thereon.

When applying coatings based on fluorine-containing vinyl polymers to provide protective coatings having a good resistance to chemical attack difficulties arise in regard to the adhesion of the coating to the substrate, according to the coating material used. For example, particular difficulties may arise in applying polyvinylidene fluoride dispersion coatings to various metal substrates in such a manner that the coatings adhere satisfactorily.

It has been proposed to produce adherent coatings from polymerisation products of vinylidene fluoride ($\text{CH}_2=\text{CF}_2$) in combination with suitable synthetic resins containing polar groups, e.g. homopolymers and copolymers of various acrylic monomers, polyvinyl esters, polyvinyl dioxalanes, polyethers, polyketones, polyamides as well as hardenable syn-

thetic resins, such as polyesters, alkyd resins and similar products.

In existing processes, it is often necessary to apply an adhesion-promoting agent to the substrate prior to the application of polyvinylidene fluoride in order to ensure satisfactory adhesion of the polyvinylidene coating to the base. The adhesion-promoting agent is however generally limited to those resins which do not lose their adhesion-promoting properties when stoved several times, for example epoxy resins.

According to another proposal, mixtures of polyesters and polyvinylidene fluoride can be applied to metal substrates. However, this technique is confined to the whirl sinter process.

Moreover, known coatings often exhibit different adhesion properties on different metal substrates. Thus, it is often necessary to prepare coating compositions having a specific formulation for each metal in order to obtain satisfactory properties, particularly adhesion values.

It is an object of the present invention to provide a new and advantageous coating composition for the preparation of protective coatings.

Thus according to one feature of the present invention we provide coating compositions comprising:—

5 A) a thermosetting polyester resin derived at least in part from at least one polyhydric alcohol, the hydroxyl group content of which is constituted by at least 80% of primary hydroxyl groups, and from at least one aromatic polycarboxylic acid and at least one aliphatic polycarboxylic acid;

B) a thermosetting acrylate resin; and

10 C) a homopolymer and/or a copolymer of a vinyl monomer containing up to two fluorine atoms.

Upon application of the above defined coating composition to a substrate, the polar groups contained in synthetic resins A and B, react with the polyvinyl compound containing fluorine, for example polyvinylidene fluoride, and at the same time an intimate link with the substrate is achieved. Coating compositions prepared in accordance with the present invention have been found to have excellent adhesion to different metal surfaces. If however the polyester resin component A) contains only aromatic or aliphatic polycarboxylic acids brittle or soft films are obtained.

25 The polyester resin A) employed in the compositions according to the present invention is preferably one containing free hydroxyl, carboxyl or other reactive groups, e.g. pseudo isocyanate or similar groups, suitable for cross-linking with thermosetting acrylate resins, for example polyesters with a hydroxyl number of at least 20, advantageously 70 to 130, and an acid number not exceeding 50, preferably 10 to 20. The polyester resin A) may be saturated or unsaturated. When such resins principally contain saturated constituents, such constituents are preferably at least trifunctional, for example at least trihydric alcohols and/or at least tribasic carboxylic acids. The acid constituents of the polyester resins are aliphatic and aromatic polycarboxylic acids, for example o-phthalic acid, isophthalic and terephthalic acid, pyromellitic acid, trimellitic acid, succinic acid, adipic acid, azelic acid, sebacic acid, dichlorosuccinic acid tetrahydrophthalic acid, tetrachlorophthalic acid, hexachloroendomethylene, tetrahydrophthalic acid also maleic acid, fumaric acid, and itaconic acid. Preferred polyhydric alcohol constituents of the polyester resins A) include for example diols and triols, such as ethylene glycol, diethylene glycol, triethylene glycol, 1,3-propane diol, 1,3-butane diol, 1,5-pentane diol, 2,2-dimethyl-1,3-propane diol, glycerin (but only in minor quantities), trimethylolmethane or propane, cyclic alcohols such as dimethylolcyclohexane and mixtures of such alcohols.

60 The molar ratio of the aromatic and aliphatic polycarboxylic acids in the polyester resin A) is conveniently in the range of 5:1 to 1:4, advantageously 3:1 to 1:3. The alcohol groups in the polyhydric alcohol residues of the polyester are advantageously constituted

by at least 90%, preferably at least 95% of primary alcohol groups. The polyester is preferably derived from a polyhydric alcohol containing exclusively primary alcohol groups. Preferred pseudo - isocyanate components for use in the polyester resins include for example adducts of aromatic isocyanates with phenols or acetoacetic ester, malonates, adducts of isocyanates, trimethylolpropane and phenol or a uretdione group-containing di-isocyanate derived from 2,4-di-isocyanatotoluene and trialkyl or alkylaryl-phosphones.

Particularly suitable coating agents are those with polyester resins A) containing at least 15% by weight, based on the polyester resin, of an aromatic polycarboxylic, preferably dicarboxylic acid.

Constituent A) of the compositions according to the present invention can be modified with the aid of fatty acids or fatty oils, e.g. in an amount of up to 25% by weight (based on the total resin). Examples of preferred fatty acids include saturated fatty acids, such as caproic acid, 2-ethyl hexoic acid, pelargonic acid, capric acid, lauric acid, myristic acid as well as branched fatty acids, such as iso-octanoic acid or iso-nonanoic acid, fatty acids produced during the refining of fats and oils, such as the so-called "pre-run fatty acids", as well as cyclohexane monocarboxylic acid.

Examples of preferred thermosetting acrylate resins in the compositions according to the present invention include homopolymers or copolymers of acrylic monomers forming reactive side groups (e.g. hydroxyl, epoxide and/or carboxyl groups, preferably methylol or methylol ether groups) in the polymer. These resins can of course be self-cross-linking, i.e. thermosetting without the addition of a hardener, or cross-linking with the aid of an auxiliary agent, i.e. hardenable with the aid of a hardener.

One of the principal constituents of preferred self-cross-linking acrylate resins B) are N-methylol amide groups combined with acrylic or methacrylic acid and/or units of maleic, fumaric and/or itaconic acid, or etherification products thereof with alcohols containing up to 8 C atoms in the alkyl group. Instead of or in conjunction with the alkylol amide groups, the self-cross-linking resins B) may also contain hydroxy alkyl esters of the above carboxylic acids wherein ester groups advantageously contain two to eighteen, preferably two to four carbon atoms, examples of such compounds including hydroxy-ethyl, 2- or 3-hydroxy-propyl and 4-hydroxy-butyl esters, such as hydroxy-ethyl acrylate or methacrylate, 2-hydroxy-propyl acrylate or methacrylate and 4-hydroxy-butyl acrylate or methacrylate and the mono-esters or diesters of the above dicarboxylic acids with polyhydric alcohols preferably with vicinal OH groups. However, the first mentioned type of self-cross-linking system with the alkylol

amide groups is generally more suitable for the self-cross-linking resins since it produces the optimum properties and facilitates the hardening of these resins. The self-cross-linking acrylate resins and those cross-linking with the aid of an auxiliary agent preferably also contain alkyl esters of acrylic or methacrylic acid containing 1 to 18, preferably 1—8 carbon atoms in the alkyl residue and, optionally, additional polymerisable monomers, such as styrene or similar products. In many cases, due to the copolymerisation of free α , β -olefinic unsaturated mono and/or polycarboxylic acids or partial esters of these polycarboxylic acids, the acrylate resins contain free carboxyl groups, whereby the acid number advantageously does not exceed 50.

The self-cross-linking acrylate resins can also be cross-linked with the aid of hardeners.

Acrylate resins cross-linking with the aid of an auxiliary agent differ from self-cross-linking acrylate resins in that they do not generally contain alkylol amide groups. Thus, an additional agent, preferably an amine resin, is generally used for hardening.

The polymer C) employed in the compositions according to the present invention is derived from a vinyl monomer containing up to two fluorine atoms, such as 1-fluoroethylene (polyvinyl fluoride) and 1,1-difluoroethylene (polyvinylidene fluoride). The polymer can be produced by any convenient polymerisation process, such as suspension or emulsion polymerisation. The fluorine content of such polymer normally amounts to from 30 to 60% by weight, preferably at least 40% by weight. Constituent C) is conveniently employed in the form of a solid, for example a powder.

The ratio of the acrylic resin constituent B) to the polyester resin constituent A) in the coating compositions according to the invention advantageously ranges from 5:1 to 1:5, preferably from 2:1 to 1:2. The ratio of constituents (A+B) to constituent C) is advantageously from 9:1 to 1:9, preferably from 3:1 to 1:3. According to a preferred embodiment of the present invention, the coating compositions according to the invention contain 2 to 25, preferably 3 to 20% by weight of constituent A, 2 to 25, preferably 3 to 20% by weight of constituent B) and 1 to 65, preferably 8 to 50% by weight of constituent C (all based on the solid resin). The total content of the three binders should preferably not exceed 60, preferably 50% by weight of the coating composition.

The coating compositions according to the present invention can, if desired, also contain additional resins, for example resins which, upon hardening, form elastic films or have a cross-linking effect, it being understood that such resins should not have any adverse effect on the properties of the coating, e.g. as regards to colour or weather resistance. For example, an addition of amine resins with

methylol or methylol ether groups, as a cross-linking constituent, may be appropriate in some cases, particularly when using thermosetting acrylate resins which are cross-linkable with the aid of an auxiliary agent. Examples of such amine resins include urea-formaldehyde resins, benzoguanamine-formaldehyde resin, as well as their etherification products, preferred resins being melamine-formaldehyde resins, particularly hexamethoxymethyl melamine.

In view of the low solubility of constituent C, the coating composition according to the invention is conveniently prepared in the form of a dispersion in polar organic solvents of high boiling point e.g. 150 to 300°C., such as dimethyl phthalate, the monomethyl-, -ethyl-, -butyl ether of ethylene glycol or their acetic esters, diethylene glycol-monoethyl-butyl ether, propylene glycol carbonate, butyrolactone and diacetone alcohol. In order to control the viscosity of the compositions, these solvents can be blended with for example, a small proportion of solvents of low boiling point which can be polar such as methyl ethyl ketone, methyl-isobutyl ketone, acetone or toluene, or with mixtures of aliphatic and aromatic hydrocarbons having a boiling point ranging from 150 to 220°C (known under the trademark "Solvesso"). The advantage of a higher boiling point for the solvent is that it enables the solvent to remain in the coating during stoving until a homogeneous film has formed.

According to a further feature of the present invention we provide a method of providing a substrate with a coating which comprises applying a coating composition as hereinbefore defined to the surface of a substrate and subsequently curing the applied composition to form a coating on the substrate.

The coating agent can be applied to the substrate in conventional manner, for example by spraying, dipping, flooding, brushing, rolling or powder coating.

The coating composition according to the invention may, if desired, contain conventional additives, such as dyestuffs, pigments, fillers, plasticizers, stabilisers, wetting agents, dispersion agents, anti-settling agents and flow agents e.g. in the usual quantities.

The use of dyestuffs and pigments is particularly appropriate if the coating composition according to the invention is to be used as a varnish. In this case, the ratio of binder (solids) to the total quantity of pigment advantageously ranges from 8:1 to 1:1, preferably from 5:1 to 3:1. Suitable dyestuffs or pigments are those capable of standing the heating conditions during curing of the coating compositions without any adverse effects, for example titanium dioxide, graphite, zinc chromate, strontium chromate, chromium oxide, zinc sulphide, nickel titanium yellow, chrome titanium yellow, cadmium yellow, cadmium red, ultra-marine blue, iron oxide red,

iron oxide black, phthalocyanine complexes and naphthol red. The dyestuffs can be organic or inorganic.

5 Fillers which may be employed in the compositions include for example talc, mica, china clay, quartz powder, barium sulfate, asbestos powder and ground slate. Convenient anti-settling agents include for example finely dispersed silicic acid, bentonite and colloidal silicates.

10 The coating compositions applied to the substrate can be solidified or hardened at high temperature, preferably above 130°C in certain cases up to 350°C, the stoving period being principally dependent on various factors such as temperature, type of base, stove dimensions, as well as composition of the coating compositions or solvents.

20 Substrates to which the coating compositions according to the invention may be applied include for example earthenware, ceramics, glass, plastics, but preferably metal, such as iron, zinc, copper, aluminium, steel, brass and bronze. The substrates can also be rendered more adhesive or more resistant to corrosion by means of mechanical and/or chemical pretreatments. But the coating compositions according to the invention adhere most satisfactorily to various metal bases, without any adhesion-promoting primer or intermediate coat. The excellent adhesion of these single coat systems corresponds to the values GT 0A to GT 1A according to the test specifications of DIN 53 151. In addition, the coatings are easy to form, show a high gloss, excellent resistance to yellowing, and weather resistance.

40 The coating compositions according to the invention can be used for the production of clear or pigmented coats, particularly for the inside and outside lining of objects coming in contact with abrasive media or atmospheric agents, for domestic appliances, machinery, vehicle components, electrical engineering components as well as for objects exposed to heat.

50 In view of their good properties, the coating compositions according to the invention are eminently suitable for use in single coating systems preferably continuous coil coating methods. These precoated sheets can subsequently be shaped by means of deep drawing, bending, profiling or embossing, without affecting the remaining properties to any appreciable extent. The adhering coating can remain as it is, but can also serve as an intermediate coat, i.e. as a base for further coats, which can consist of the same or another standard coating material.

60 According to a still further feature of the present invention we provide a process for preparing a coating composition as hereinbefore described in the form of a dispersion, which comprises mixing a solution or dispersion of components A) and B) or separate

solutions or dispersions of components A) and B) with component C) in the form of a dispersion or a powder.

70 The coating compositions according to the invention may be produced by mixing constituents A, B and C, constituents A and B being conveniently employed as resin solutions in organic solvents, whilst constituent C, such as polyvinylidene fluoride, conveniently employed as a solid, for example in dispersion, but in most cases as a powder. Grinding is preferably particularly thorough, being effected for example in a ball mill. Constituents A, B and C and any additives such as pigments and fillers, including an additional resin, if applicable, can be added in any desired order prior to grinding. For example, constituent C can be ground or dispersed together with constituent A or B or both. It is also possible to disperse constituent C in a solution or dispersion of at least one of constituents A and B. The amine resin, if any, may be added after dispersing.

90 For a better understanding of the invention the following Examples are given by way of illustration only. In the Examples the parts quoted are parts by weight. As far as the roller application of Examples 1 to 4 is concerned, a solvent mixture A is used consisting of 25 parts dimethyl phthalate, 25 parts diethylene glycol monoethyl ether, 25 parts 2-ethoxyethyl acetate and 25 parts 3,5,5-trimethylcyclohex-2-en-1-one. For spraying, a solvent mixture B is used consisting of 10 parts dimethyl phthalate, 40 parts 3,5,5-trimethylcyclohex-2-en-1-one, 25 parts methyl ethyl ketone, 10 parts 2-ethoxy-ethyl acetate and 15 parts butyl acetate.

Example 1.

105 A mixture of 303 g polyvinylidene fluoride, 70 g thermosetting polyester resin (composed of 39.8% parts by weight isophthalic acid, 20.4% parts by weight sebacic acid, 28.4% parts by weight, 2,2-dimethyl-1,3-propane diol and 11.4% parts by weight trimethylol propane) 30.5 g thermosetting acrylate resin (composed of 56.7 parts methacrylic acid, 60.7 parts acrylic acid, 308.5 parts N-butoxymethyl methacrylamide, 96.5 parts N-butoxymethyl acrylamide, 130.6 parts 4-hydroxybutyl methacrylate, 87.5 parts 2-hydroxypropyl acrylate and 259.5 parts styrene) and 596 g of solvent mixture B is applied to a 0.3 to 0.5 mm thick tin plate by spraying to a coat thickness (wet film thickness) of 50 to 150 microns and cured for 15 minutes at 180°C. This results in a colourless, satisfactorily adhering and elastic coating.

Example 2.

125 A mixture of 89.4 g polyvinylidene fluoride, 80 g thermosetting polyester resin (composed of 36.4 parts terephthalic acid, 11.1 parts ethylene glycol, 16 parts 2,2-dimethyl-1,3-

propane diol, 13.1 parts trimethylol propane, 8.2 parts pelargonic acid and 15.2 parts maleic acid anhydride) 186 g thermosetting acrylate resin (composed of 27.2 parts acrylic acid, 35 parts methacrylic acid, 250.7 parts 2-hydroxypropyl acrylate, 241 parts 4-hydroxybutyl methacrylate, 219.6 parts butyl methacrylate and 226.5 parts styrene), 89.4 g talc and 555 g solvent mixture A is applied onto steel sheet by rolling to a wet film thickness of about 50 to 100 microns and cured for 10 minutes at 190°C. The cured coating is then covered with an additional 100 micron coat consisting of a stoving varnish based on an alkyd resin modified with the aid of a non-drying fatty acid and a melamine resin partly etherified with the aid of butanol (mixture ratio 7:3) by means of spraying and cured for 30 minutes at 140°C. This produces a paint of excellent adhesion, good quality surface and good elasticity.

Example 3.

A mixture of 187.6 g polyvinylidene fluoride, 73 g thermosetting polyester resin (as defined in Example 2) 60 g thermosetting acrylate resin (as defined in Example 1) 57 g titanium dioxide, 31 g talc and 591 g of solvent mixture A is applied to a base of phosphated steel sheet by rolling to a wet film thickness of 50 to 100 micron and cured for 6 minutes at 195°C. The cured coating is covered by a further coating agent consisting of 185 g polyvinyl fluoride, 85 g thermosetting polyester resin as in Example 1, 84 g thermosetting acrylate resin as in Example 1, 90 g titanium dioxide and 556 g of solvent mixture B by spraying to a wet film thickness of 50 to 150 microns and cured in a stoving-circulating air oven for 2 minutes at 240°C. This produces a satisfactorily adhering, glossy, elastic and corrosion-resistant coating of perfect adhesion to the base.

Example 4.

A mixture of 167.4 g polyvinylidene fluoride, 73.7 g thermosetting polyester resin (as in Example 1) 93.7 g thermosetting acrylate resin (as in Example 1) 83.5 g titanium dioxide and 582 g of solvent mixture A is applied to a base of 0.5 to 0.8 mm thick aluminium sheet by rolling to a wet film thickness of 50 to 100 microns and cured for 3 minutes at 230°C. This produces an elastic, glossy and corrosion-resistant coating adhering well to the substrate which can sub-

sequently be subjected to deep drawing, bending or similar processes, without any adverse effect.

Comparative compositions

a) A coating composition is prepared as in Example 4 except that instead of the specified alcohols, 32.1 parts by weight of glycerine are employed.

b) A coating composition is prepared as in Example 4 except that the polyester resin is derived exclusively from 56.2 parts by weight of isophthalic acid and 31.9 parts by weight of glycerine.

The coating compositions of the two comparative tests are applied to an aluminium sheet substrate as in Example 4 and cured.

Test results of the comparative compositions

1. Extension adhesiveness

The coated aluminium plates produced according to Example 4 and using comparative compositions a) and b) are treated as follows: A so-called lattice cut is made in the coating the depth of the cut extending to the metal, and the sample is then stretched at the cut point. A pressure-sensitive adhesive strip is then pressed onto the stretched lattice cut point and then rapidly removed from the sample. If on removing the strip the coating adheres to the adhesive strip and not to the plate then the adhesion of the coating is poor. If the coating cannot be removed from excellent adhesion.

2. Flexibility

To ascertain the flexibility the plates coated according to Example 4 are bent by 180° in such a way that the coating is located on the outside (so-called T-bend test).

3. Thermal stability

To test the thermal stability in each case three samples of the coated plates were hardened at different temperatures and for varying periods of time, namely 3 minutes at 230°C, 2 minutes at 270°C and 1 minute at 300°C. By means of these stoving conditions the conditions necessary for continuous coil coating are approximately reproduced.

4. Yellowing resistance

The yellowing resistance is measured on the same samples as used for the thermal stability test. It is determined visually whereby the following assessment applies:

No change in the white shade	= excellent
Slight yellowing	= average
Pronounced yellowing	= poor

The following Table summarises the results of the comparative tests.

TABLE

Characteristics	Sample	Stoving conditions		
		3 min./230°C	2 min./270°C	1 min./300°C
Extension adhesiveness	4	excellent	excellent	excellent
	a (comparison)	average	poor	poor
	b (comparison)	poor	poor	poor
Flexibility	4	excellent	excellent	average
	a (comparison)	poor	poor	poor
	b (comparison)	poor	poor	poor
Yellowing resistance	4	excellent	excellent	excellent
	a (comparison)	average	poor	poor
	b (comparison)	poor	poor	poor

The Table shows that the coating compositions according to the invention at stoving temperatures of 230 to 300°C retain their excellent flexibility, extension adhesiveness and yellowing resistance. Thus at stoving temperatures of 270 and 300°C under the indicated conditions no yellowing occurs.

In comparison comparative samples a) the polyester component of which contains aromatic and aliphatic carboxylic acids but an alcohol component with only 66% primary hydroxyl groups, after curing at 230°C revealed a reduction of the extension adhesiveness, the yellowing resistance as well as poor flexibility. At even higher stoving temperatures a further deterioration in these characteristics occurred.

Samples b) the polyester resin components of which consisted exclusively of an aromatic acid and glycerine with only 66% primary hydroxyl groups, exhibited poor characteristics even at the stoving temperature of 230°C, and these are maintained at higher stoving temperatures.

WHAT WE CLAIM IS:—

1. Coating compositions comprising:—
 - A) a thermosetting polyester resin derived at least in part from at least one polyhydric alcohol, the hydroxyl group content of which is constituted by at least 80% of primary hydroxyl groups, and from at least one aromatic polycarboxylic acid and at least one aliphatic polycarboxylic acid;
 - B) a thermosetting acrylate resin; and
 - C) a homopolymer and/or a copolymer of

a vinyl monomer containing up to two fluorine atoms.

2. Compositions as claimed in claim 1 wherein the polyester of component A) has a hydroxy number of at least 20 and an acid number of at most 50.

3. Compositions as claimed in claim 1 or 2 wherein the polyester of component A) has a hydroxy number between 70 and 130.

4. Compositions as claimed in any of the preceding claims wherein the polyester of component A) has an acid number of 10 to 20.

5. Compositions as claimed in any of the preceding claims wherein the polyester of component A) contains at least 15% by weight (based on the polyester resin) of units of an aromatic polycarboxylic acid.

6. Compositions as claimed in claim 5 wherein the said aromatic polycarboxylic acid is a dicarboxylic acid.

7. Compositions as claimed in any of the preceding claims wherein the molar ratio of the aromatic and aliphatic polycarboxylic acids in component A) is in the range of 5:1 to 1:4.

8. Compositions as claimed in any of the preceding claims wherein the molar proportion of the aromatic to aliphatic polycarboxylic acids in component A) is in the range of 3:1 to 1:3.

9. Compositions as claimed in any of the preceding claims wherein the hydroxyl group content of the polyester resin A) is constituted by at least 90% of primary hydroxy groups.

10. Compositions as claimed in claim 9

wherein the hydroxyl group content of the polyester component A) is constituted by at least 95% of primary hydroxy groups.

11. Compositions as claimed in claim 9
5 or 10 wherein the hydroxyl group content of polyester component A) is constituted exclusively by primary hydroxyl groups.

12. Compositions as claimed in any of the preceding claims wherein the polyester of component A) contains up to 25% by weight
10 (based on component A) of units of a saturated fatty acid.

13. Compositions as claimed in any of the preceding claims wherein component B)
15 contains monomer units having reactive side-chains.

14. Compositions as claimed in claim 13 wherein component B) contains monomer units having hydroxy, alkylol, epoxide and/
20 or carboxylic groups.

15. Compositions as claimed in any of the preceding claims wherein component B) contains α,β -olefinically unsaturated carboxylic acid amide monomer units.

16. Compositions as claimed in any of the preceding claims wherein component B) contains acryl- or methacryl alkylol amide monomer units.

17. Compositions as claimed in claim 16 wherein the alkylol groups of the alkylol amide are etherified by an alcohol having
30 up to 8 carbon atoms.

18. Compositions as claimed in any of the preceding claims wherein component B) contains monomer units of at least one
35 hydroxyalkyl ester of an α,β -olefinically unsaturated carboxylic acid with an alcohol containing 2 to 18 carbon atoms.

19. Compositions as claimed in claim 18 wherein the alcohol contains 2 to 4 carbon
40 atoms.

20. Compositions as claimed in claim 18 or 19 wherein the hydroxy-alkyl ester is an ester of an acrylic or methacrylic acid.

21. Compositions as claimed in any of the preceding claims wherein component B) contains monomer units of a partial ester of a polyhydric alcohol with an unsaturated
45 carboxylic acid.

22. Compositions as claimed in any of the preceding claims wherein component B) contains units of a hydroxyalkyl ester of a polyhydric alcohol having vicinal hydroxy groups.

23. Compositions as claimed in any of the preceding claims wherein component B) contains units of maleic, fumaric and/or
55 itaconic acid.

24. Compositions as claimed in any of the preceding claims wherein component B) has an acid number of up to 50.

25. Compositions as claimed in any of the preceding claims wherein component B) contains monomer units of an alkyl ester of acrylic or methacrylic acid with an alkanol
65 having 1 to 18 carbon atoms.

26. Compositions as claimed in claim 25 wherein the said alkanol contains 1 to 8 carbon atoms.

27. Compositions as claimed in any of the preceding claims wherein component B) contains styrene monomer units. 70

28. Compositions as claimed in any of the preceding claims wherein component B) is self-cross-linking, or thermosetting in the presence of a hardener. 75

29. Compositions as claimed in any of the preceding claims wherein component C) comprises polyvinyl fluoride and/or polyvinylidene fluoride.

30. Compositions as claimed in any of the preceding claims wherein component C) has a fluorine content from 30 to 60% by weight. 80

31. Compositions as claimed in claim 30 wherein component C) has a fluorine content of at least 40% by weight. 85

32. Compositions as claimed in any of the preceding claims wherein component C) is employed as a solid substance.

33. Compositions as claimed in claim 32 wherein component C) is employed as a powder. 90

34. Compositions as claimed in any of the preceding claims wherein the weight ratio of components A) and B) to component C) is in the range of 9:1 to 1:9. 95

35. Compositions as claimed in claim 34 wherein the weight ratio of components A) and B) to component C) is in the range of 3:1 to 1:3. 100

36. Compositions as claimed in any of the preceding claims wherein the weight ratio of component A) to component B) is in the range of 5:1 to 1:5.

37. Compositions as claimed in any of the preceding claims wherein the weight ratio of component A) to component B) is in the range of 2:1 to 1:2. 105

38. Compositions as claimed in any of the preceding claims comprising 2 to 25% by weight of component A), 2 to 25% by weight of component B) and 1 to 65% by weight of component C), the total weight of components A), B) and C) being not more than 60% by weight of the composition. 115

39. Compositions as claimed in claim 38 comprising 3 to 20% by weight of component A) 3 to 20% by weight of component B) and 8 to 50% by weight of component C), the total weight of components A), B) and C) being not more than 50% by weight of the composition. 120

40. Compositions as claimed in any of the preceding claims further containing an amino resin. 125

41. Compositions as claimed in claim 40 wherein the said amino resin is an etherified amino resin.

42. Compositions as claimed in claim 40 or 41 wherein the amino resin is one capable 130

of effecting curing of component B).

43. Compositions as claimed in any of claims 40 to 42 wherein the amino resin is an ureaformaldehyde resin, a benzoguanamine-formaldehyde resin or a melamine-formaldehyde resin.

44. Compositions as claimed in any of the preceding claims wherein the composition is in the form of a dispersion.

45. Compositions as claimed in claim 44 in the form of a dispersion of components A), B) and C) in a polar organic solvent having a boiling point or boiling range such that the solvent is retained in the coating during its curing for such time until a homogeneous film is formed.

46. Compositions as claimed in claim 44 or 45 wherein the polar organic solvent has a boiling point between 150 and 300°C.

47. Compositions as claimed in claims 44 to 46 wherein the dispersion additionally contains a minor amount of a lower-boiling solvent or a solvent mixture of aliphatic and aromatic hydrocarbons having a boiling point in the range 150 to 220°C.

48. Compositions as claimed in any of the preceding claims further containing one or more dyes, pigments, fillers, plasticizers, stabilisers, wetting agents, dispersing agents and anti-settling agents or flow-improving agents.

49. Compositions as claimed in any of the preceding claims wherein the weight ratio of the solids components A), B) and C) to the total of pigments is 8:1 to 1:1.

50. Compositions as claimed in claim 48 wherein the said weight ratio is 5:1 to 3:1.

51. A composition as claimed in claims 1 to 50 substantially as described herein.

52. A composition as claimed in claims 1 to 50 substantially as described herein with reference to the Examples.

53. A process for preparing a coating composition as claimed in any of the preceding claims in the form of a dispersion, which comprises mixing a solution or dispersion of components A) and B) or separate solutions or dispersions of components A) and B) with component C) in the form of a dispersion or a powder.

54. A process as claimed in claim 53 wherein the solution or dispersion of components A) and B) is prepared by mixing a solution or dispersion of component A) with a solution or dispersion of component B).

55. A process as claimed in claim 53 or claim 54 wherein the said solution of component A) and/or component B) comprises an organic solvent.

56. A process as claimed in any of claims 53 to 55 wherein the mixing is performed in a ball mill.

57. A process as claimed in any of claims 53 to 56 wherein an amino resin is added

after dispersing the components.

58. A process as claimed in any of claims 53 to 57 substantially as described herein.

59. A process as claimed in claims 53 to 57 substantially as described herein with reference to the Examples.

60. A coating composition whenever prepared by a process as claimed in any of claims 53 to 59.

61. A coated article which comprises a coating derived from a coating composition as claimed in any of claims 1 to 52.

62. A method of providing a substrate with a protective coating which comprises applying a coating compositions as claimed in any of claims 1 to 52 to the surface of a substrate and subsequently curing the applied composition to form a protective coating on the substrate.

63. A method as claimed in claim 62 wherein the protective coating is applied by a one-step coating process.

64. A method as claimed in claim 63 wherein the protective coating is applied by a continuous coil-coating process.

65. A method as claimed in any of claims 62 to 64 wherein the curing of the composition is effected at a temperature above 130°C.

66. A method as claimed in any of claims 62 to 65 wherein the curing of the composition is effected at a temperature up to 350°C.

67. A method as claimed in any of claims 62 to 66 wherein the resulting coating is subsequently provided with a further coating.

68. A method as claimed in any of claims 62 to 67 wherein the coating composition is applied to the substrate by spraying, dipping, flooding, brushing, rolling or powder coating.

69. A method as claimed in any of claims 62 to 68 wherein the substrate is rolled in the said coating composition in a solvent mixture comprising dimethyl phthalate, diethylene glycol monoethyl ether, 2-ethoxyethyl acetate and 3,5,5-trimethylcyclohex-2-en-1-one.

70. A method as claimed in any of claims 62 to 68 wherein the substrate is sprayed with the said coating composition in a solvent mixture comprising dimethylphthalate, 3,5,5-trimethyl-cyclohex-2-en-1-one methyl ethyl ketone, 2-ethoxyethyl acetate and butyl acetate.

71. A method as claimed in any of claims 62 to 70 wherein the surface of the substrate is composed of earthenware, ceramics, glass, plastics or metal.

72. A method as claimed in claim 71 wherein the surface of the substrate is composed of iron, zinc, copper, aluminium, steel, brass or bronze.

73. A method as claimed in claim 62 substantially as herein described.

74. A method as claimed in claim 62

substantially as herein described with reference to any of the Examples.

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